NOV 22 '85

431-L-12

EP1.89/2:600/52-85/093

United States
Environmental Protection
Agency

Water Engineering
Research Laboratory
Cincinnati OH 45268

Research and Development

EPA/600/S2-85/093 Sept. 1985

EPA

# Project Summary

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# Prediction of Selectivity for Activated Carbon Adsorption of Trace Organic (Homologue) Contaminants

ORIGIN

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**Preferential adsorption of organic compounds onto activated carbon from dilute aqueous solutions was studied to develop a comprehensive theoretical basis for predicting adsorption of multicomponent solutes. The study compared different carbons and investigated their adsorption behavior with variable aqueous solution properties, and the differences between gas and liquid phase adsorption. The overall objective was to develop and test the comprehensive solvophobic theory.**

**Experimental adsorption isotherms of a series of alcohols on five different carbons were measured and compared. Isotherms were run for 4-n-propyl phenol at various concentrations of ammonium sulfate salt and methanol as the additives to increase or decrease surface tension of solution, respectively. Also, isotherms for three linear carboxylic acids were measured at different pH's to determine the effect on adsorption.**

**An experimental glass vacuum system has been designed and built to measure adsorption isotherms in the gas phase. Measurements of adsorption isotherms for four alcohols were conducted in the aqueous and gas phases and confirmed the theoretical model.**

**Predictive techniques for multicomponent adsorption were developed based on the use of an equation of state. They were compared with the Ideal Adsorbed Solution (IAS) theory using competitive phenol adsorption data.**

***This Project Summary was developed by EPA's Water Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).***

## Background

Although activated carbon (AC) adsorption has been widely used for odor and color removal in the water industry, only recently has it been seriously considered for removal of dissolved organics from water supplies. This recent interest is caused primarily by the growing concern for potential carcinogenic, mutagenic, and teratogenic compounds found in drinking waters.

With respect to solid-liquid adsorption, a major limitation of the various equilibrium theories of adsorption (besides the adaptation of the partial solubility parameter theory) is that they were orginally derived from gas and vapor phase adsorption and thereby *a priori* ignored the presence of the solvent during solute adsorption.

Recent attempts to include the solvent effect in aqueous phase adsorption include a semi-empirical approach based on partial solubility parameters called the net adsorption energy approach. Unfortunately, the arbitrary choice of the relative values for the acid and base hydrogen bonding solubility parameters is without theoretical justification and renders this approach somewhat capricious.



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During the past several years, a concerted effort has been made in our Rensselaer Polytechnic Institute laboratory to understand the role of the solvent during liquid-solid approach. A theoretical basis has been derived for predicting *a priori* the preferential adsorption of organic compounds in the same homologous series on activated carbon from dilute aqueous solution. This basis has been derived and used with confidence to rank-order single solute isomers (alcohols, ketones, and phenols) with respect to their adsorption potential. Clearly, the ability to predict the effects of structure on the adsorption of organic molecules between different homologous series from dilute aqueous solutions could be of great value in the design and operation of large-scale commercial plants.

## Objectives

The objectives of this study were as follows:

1. To compare different activated carbons using a well characterized, model homologous series (linear alcohols),
2. To evaluate the effects of surface tension on adsorption by changing the concentration of ammonium sulfate salt and methanol,
3. To evaluate the effects of pH on carboxylic acids adsorption,
4. To develop further the comprehensive solvophobic theory by estimating the value of the gas phase term. This involved measuring the gas phase adsorption of the same homologous series as that measured from the liquid phase, and
5. To develop predictive techniques based on the use of an equation of state for multicomponent adsorption from mixtures.

Adsorption capacity for specific, single, organic solutes of a homologous series is thought to be a direct function of: (1) the adsorbate properties, (2) the solution conditions, and (3) the nature of the adsorbent. Little quantitative information is known about the surface characteristics of carbon, the solution properties, and their influence on organic adsorptive selectivity. The general thrust of this study is to extend both the theoretical formulations and the experimental data base to develop a comprehensive theoretical basis including the important factors on adsorption for predicting *a priori* the preferential adsorption of organic compounds on activated carbon from aqueous solution.

## Materials and Methods

### *Adsorbents and Adsorbates*

Crushed granular activated carbons (PAC) were the major adsorbents used in this study. Comparisons were made of adsorption isotherms of three aliphatic alcohols on five different granular activated carbons. Cleaning procedures of the PAC were an important aspect of obtaining reproducible isotherms.

The adsorbates used included three homologous series of alkyl phenols, aliphatic alcohols, and linear carboxylic acids—all of the highest grade available (>99% purity). Stock solutions of the individual alcohols or phenols were made up with standard 0.01 m phosphate buffer (pH 7.00) and stored in amber glass or aluminum-covered bottles. Carboxylic acids were prepared in phosphate buffer solutions of pH 4.75 and 7.00.

For the liquid phase, several innovations have been introduced into the adsorption isotherm procedures in an attempt to improve reproducibility and accuracy and to reduce solute losses. Thus completely filled and capped stainless steel tubes containing the adsorbate/adsorbent mixture were rotated 360° end-over-end at 2 rpm for 24 hr at 20 ± 0.5°C. The tubes were then ultracentrifuged at 20,000 rpm for 20 to 30 min at 20°C, thereby spinning down the carbon. The tubes were then opened, and the supernatant was analyzed directly.

### *Vacuum System*

The vacuum system (made of glass) was used in the gas phase adsorption/desorption experiments. The amount of alcohol adsorbed onto the activated carbon was measured directly using an electrobalance. The final mass of the sample and the final pressure in the system were used to represent one point on the isotherm. Successive points were determined by admitting small doses of alcohol and recording the equilibrium mass and pressure readings until the final system pressure was nearly equal to the vapor pressure of the pure alcohol. The desorption isotherm was then determined in a similar, stepwise fashion by heating and evacuating the carbon samples. Mass and pressure readings were recorded at equilibrium.

### *General Solvophobic Approach*

The solvophobic (cϕ) theory describes the tendency of a surrounding solvent medium to influence aggregation or dissociation of those molecules with considerable microsurface areas exposed to the solvent medium.

In the solvophobic treatment, adsorption is considered a reversible reaction between the adsorbate molecules, $S_i$, and the activated carbon, C, to form the adsorbed complex, $S_iC$, at the surface of the carbon, $S_i + C \leftrightarrows S_iC$. The effect of the solvent on this reaction is obtained by subtracting the standard free energy change for the reaction in the gas phase from that in the presence of the solvent (taking as standard states $X_k^\circ \equiv 1$, $p_k^\circ \equiv 1$ atmosphere ideal gas). This process results in a net free energy change, with $\Delta G^{net}_{(solvent\ effect)}$ expressing the effect of the solvent on the association adsorption reaction.

Conceptually, Sinanoglu posed a two-step dissolution process. First, a hole or cavity needs to be prepared in the solvent to accommodate the solute, carbon, or adsorbed complex molecule. Second, after the molecule is placed into the cavity, it interacts with the solvent. Quantitatively, this process is expressed as follows:

$$\Delta G^{net}_{(solvent\ effect)} = \Delta G^{assoc}_{(solvent)} - \Delta G^{assoc}_{(gas)} = RT\ \ln[k^H_{S_iC}/k^H_{S_i}k^H_C] \quad (1)$$

or

$$\Delta G^{net}_{(solvent\ effect)} = \Delta G^{net}_{j,S_iC} - \Delta G^{net}_{j,S_i} - \Delta G^{net}_{j,C} \quad (2)$$

where $K^H_k = p_k/X_k$ is the Henry's constant for the $k^{th}$ species, and j represents each type of interaction. After specifying each interaction such as the cavity, van der Waals', and electrostatic terms plus two correction terms for polymer mixing and reduced electrostatic effects because of the presence of the solvent, the following expression is obtained from Equations 1 and 2 for the overall standard free energy change, viz.

$$\Delta G^{assoc}_{(solvent)} = \Delta G^{assoc}_{(gas)} + [\Delta G_{cav} + \Delta G_{vdw} + \Delta G_{es} + \Delta G_{red}]^{net}_{S_iC-S_i-C} - RT\ \ln(RT/P_oV) \quad (3)$$



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where the last term is called the cratic term and results from an entropy or free volume reduction. $\Delta G^{assoc}_{(solvent)}$ is related to the experimental equilibrium constant, $K_{solvent,i} \equiv X_{S_iC}/X_{S_i}X_C$, which itself will be related to the experimental adsorption capacity $\bar{p}_i$ for solute $S_i$ later in this analysis. $\Delta G^{assoc}_{(gas)}$ can be calculated by multiplying the spreading pressure by the molar area occupied by the adsorbate in a surface layer, $a_i$

$$\Delta G^{assoc}_{(gas)} = -a_i\pi \qquad (4)$$

The spreading pressure can be obtained from gas phase isotherms. Each term in the square bracket in Equation 3 can be calculated explicitly from known physiochemical parameters obtained from the literature.

For the comprehensive cϕ-model, each of the terms in Equation 3 is calculated explicitly; for the simplified model, the thermodynamic microsurface area change of the reaction, ΔA, in the cavity term is assumed to be proportional to the cavity surface area, TSA, of the specific sorbate and homologous series, ΔA = g TSA. Thus in this study, ln Q°b is correlated with TSA, where Q°b is the initial slope at low solute concentration for the Langmuirian adsorption isotherm. Also, included in the comprehensive report are (1) the adsorption behavior as related to surface tension at various concentrations of ammonium sulfate salt and methanol, (2) pH effect, and (3) a comparison of a nonideal multicomponent adsorption model based on the use of an equation of state with the ideal adsorbed solution theory.

## Experimental Results

### Comparison Between Different Carbons

In Table 1, the Langmuir adsorption parameters Q° and lnQ°b are correlated for the linear alcohols with molecular weight. Very good correlations are obtained. To test the simplified version of the solvophobic theory for different carbons, the molecular cavity surface area of each solute (i.e., the total surface area, or TSA) was calculated using the MDS program. The TSA for each alkyl alcohol is then correlated with the Langmuir adsorption parameters in an attempt to verify the theory as a predictive measure of solute adsorption. In Table 1, we observe that the adsorptivities for the linear alcohols also correlate well with TSA. However, TSA does not significantly correlate with adsorption parameters any better than molecular weight for linear alcohols, as expected.

In Table 2, the Langmuir adsorption parameters Q° and lnQ°b are listed with characteristics of adsorbents for five different carbons. Neither the saturation adsorption nor the adsorption capacity has any apparent correlation with surface area of adsorbents. The surface energy of adsorbent should have an important effect on the adsorption process.

### The Differences Between Gas and Liquid Phase Adsorption

Adsorption isotherms were measured in the gas phase and in the liquid phase for four linear alcohols (butanol-heptanol) and three branched alcohols (2-methyl 1-butanol, 2-methyl 3-pentanol, 3-3-dimethyl 1-butanol) on the same activated carbon. All of these isotherms fit the Langmuir form very well, and the parameters of this model versus molecular weight of the linear alcohol appear in Figure 1. The saturated adsorption capacity, Q°, increases linearly with molecular weight for adsorption from solution, whereas the opposite is seen for gas adsorption. The amount of water adsorbed from the aqueous phase can also be estimated by assuming complete wetting of the entire carbon surface (1014 $m^2/g$). By assuming spherical molecules in hexagonal packing on the surface, we can calculate the amount of water necessary to cover the remaining surface not covered by the alcohol. The adsorption capacity for water also appears on Figure 1 and is seen to decrease linearly as the alcohol adsorption increases. Since the water curve is much higher than the solute curve, we know that the solute never forms a complete monolayer on the surface in liquid phase adsorption. The energy term, b, increases with molecular weight in all cases except one. The anomalous result for the adsorption of heptanol from the gas phase is probably caused by steric exclusion effects or incomplete adsorption, since extreme hysteresis was observed for its isotherm during desorption.

### General Solvophobic Approach

The solvent-effect free energies, $\Delta G^{net}_{solvent\ effect}$, for 12 linear and branched alcohols have been calculated previously. The gas phase free energies are

**Table 1.** *Correlation Coefficient r for Langmuir Adsorption Parameters versus Molecular Weight and Total Surface Area for the Alkyl Alchohols on Five Different Carbons*[a]

| | Filtrasorb 400 | | W20 | | D10 | | SA4 | | SA Plus | |
|---|---|---|---|---|---|---|---|---|---|---|
| Adsorption Parameter | Molecular Weight | TSA $A^2$ | Molecular Weight | TSA $A^2$ | Molecular Weight | TSA $A^2$ | Molecular Weight | TSA $A^2$ | Molecular Weight | TSA $A^2$ |
| Q° | 0.99 | 0.99 | 0.85 | 0.85 | 0.87 | 0.87 | 0.79 | 0.79 | 0.99 | 0.99 |
| lnQ°b | 0.97 | 0.97 | 0.96 | 0.94 | 0.97 | 0.97 | 0.93 | 0.93 | 0.98 | 0.98 |

[a]*The alcohols studied were butanol, pentanol, and hexanol.*

**Table 2.** *Langmuir Adsorption Parameters for the Alkyl Alcohols on Five Different Carbons*

| | | | Butanol | | Pentanol | | Hexanol | |
|---|---|---|---|---|---|---|---|---|
| Adsorbents | Surface Area ($m^2/g$) | Iodine Adsorption (mg/g) | lnQ°b | Q° (mmoles/g) | lnQ°b | Q° (mmoles/g) | lnQ°b | Q° (mmoles/g) |
| Filtrasorb | 1031 | 1200 | 1.29 | 0.18 | 2.14 | 0.44 | 4.12 | 0.78 |
| W20 | 540 | 590 | 1.36 | 0.50 | 3.41 | 0.49 | 4.16 | 0.73 |
| D10 | 530 | 580 | 1.25 | 0.55 | 3.31 | 0.62 | 3.93 | 0.62 |
| SA4 | 690 | 715 | 1.68 | 0.61 | 3.16 | 0.56 | 3.42 | 0.91 |
| SA Plus | 930 | 1040 | 2.23 | 0.35 | 2.96 | 0.60 | 3.30 | 0.86 |



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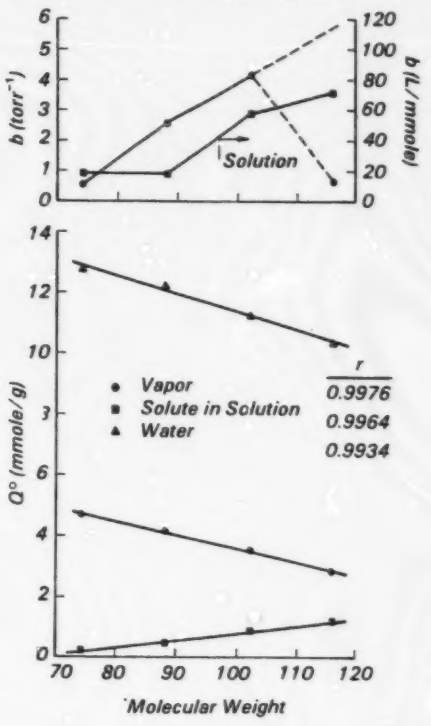


*Figure 1. Langmuir model parameters versus molecular weight for the adsorption of linear alcohols from gas and liquid phases.*

calculated using Equation 4 and added to the solvent-effect free energies to yield the free-energy change in solution (see Equation 3).

Equation 4 is shown as the theoretical line on Figure 2, and the experimental points for the four linear alcohols fall very close to this line. Figure 2 also shows the experimental points for these compounds when adsorbed from the liquid phase. The cϕ theory predicts a linear relationship between lnQ°b and SOLVENT. This is shown by the best fit line, which correlates the data quite well (r = 0.979). Thus the reversal in the order of preferential adsorption resulting from the presence of water is observed experimentally and substantiated theoretically.

For this reversal to occur, the dominant mechanism for equilibrium adsorption onto activated carbon must be different in the vapor and aqueous phases. Although little quantitative information is known about the surface characteristics of activated carbon and its influence on organic adsorptive selectivity, essentially two types of interactions are thought to dominate. The first can be characterized by van der Waals physical interactions, and it occurs on a majority of the surface (on basal planes). The second type of surface interaction, which occurs at the more reactive edges of the microcrystallites, can be characterized by attractive polar interactions resulting from, for example, hydrogen bonding and electrostatic forces. These specific interactions result from the surface heterogeneity and the presence of oxides, hydroxyls, and other groups on the surface. The adsorption capacities for alcohols are much higher for gas adsorption than for liquid phase adsorption (Figure 1). Thus gas adsorption is most likely dominated by van der Waals dispersion interactions.

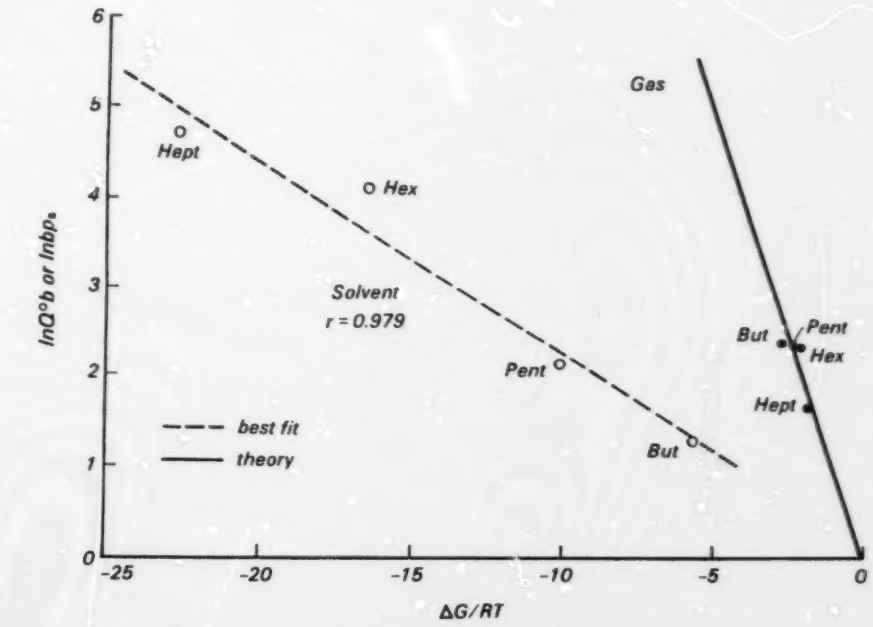


*Figure 2. lnQ°b and lnbp° as a function of $\Delta G^{assoc}_{solvent}$ and $\Delta G^{assoc}_{gas}$, respectively.*

## Surface Tension Effect on Adsorption

Adsorption isotherms were measured in the liquid phase for 4-n-propylphenol in solvents of varying surface tension. The surface tension was changed by adding varying concentrations of (1) ammonium sulfate salt to increase the solvent surface tension, or (2) methanol to decrease the solvent surface tension. Figure 3 shows the adsorption capacity, Q°, and the adsorbability, lnQ°b, as functions of salt concentration and surface tension. In both cases the first four points follow a linear increasing trend as predicted by the cϕ theory. The theory therefore fits the data well up to a certain salt concentration (around 1.143 M). Above this concentration, the data show a decrease in adsorption, deviating from the theory. This tendency may be explained by entropic effects. At high salt concentrations, the salt molecules may hinder the movement of the organic toward the carbon surface, or they may induce a precipitation. The discussion of adsorption behavior at various concentrations of methanol is also included in the comprehensive report.

## pH Effect on Adsorption

Adsorption isotherms were measured at different pH values (7.00 and 4.75) in the aqueous phase for three linear carboxylic acids on the same activated carbon. All of these isotherms fit the Langmuir form very well. A large increase in adsorbability occurred as a result of the lower pH for each acid studied. This can be explained by noting that a low pH increases the relative amount of apolar, undissociated carboxylic acid, and this relatively non-polar species is more easily adsorbed than the dissociated form.

## Multi-Component Adsorption

Figure 4 contains the experimental binary adsorption data and the predicted



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results for an initial concentration of the alkyl phenols in the mixtures. Solid lines and dotted lines are calculated using the IAS theory and the theory based on the equation of state, respectively. Agreement between predicted and experimental results is good for the latter theory using van der Waals Equation, especially in the higher surface loading region compared with that predicted by the IAS theory. The IAS theory appears to be most suitable for quantitative prediction of binary adsorption of small organic molecules with similar adsorption characteristics.

## Conclusions

The work reported here involves the development of a comprehensive theoretical basis for predicting the preferential adsorption of organic compounds onto activated carbon from dilute aqueous solution. A detailed analysis including the characteristics of adsorbents, the effect of solution properties, and the differences between gas and liquid phase adsorption yields an insight into the adsorption process. This, together with the solvophobic theory, provides a quantitative description of all the important factors on adsorption.

The solvophobic theory is tested using single-solute aqueous-phase adsorption isotherms of a series of alcohols on different carbons. Correlations with adsorption capacity for the simplified solvophobic theory parameter, absorbate molecular area (TSA), are all in good agreement with theory for all five different carbons. Despite the steric hindrance (pore size and pore size distribution), both the adsorption capacity and adsorbability show no apparent correlation with surface area of adsorbents. It seems that the surface energy of the adsorbent has an important effect on the adsorption process.

Adsorbability of 4-n-propylphenol increases linearly with increasing ammonium sulfate concentration (or surface tension) up to a critical concentration of about 1.143 M. At higher concentrations the adsorbability decreases, deviating from the theory. This result is explained by incomplete adsorption and precipitation arguments. Adsorbability decreases linearly with the volume percent of methanol present in the solvent. Solvent surface tension is not a linear function of methanol concentration, so adsorbability does not correlate linearly with surface tension. The variability of the parameter $\kappa^{\phi}$ in the solvophobic theory is invoked to explain this result; however, competitive effects resulting from the methanol may also be present.

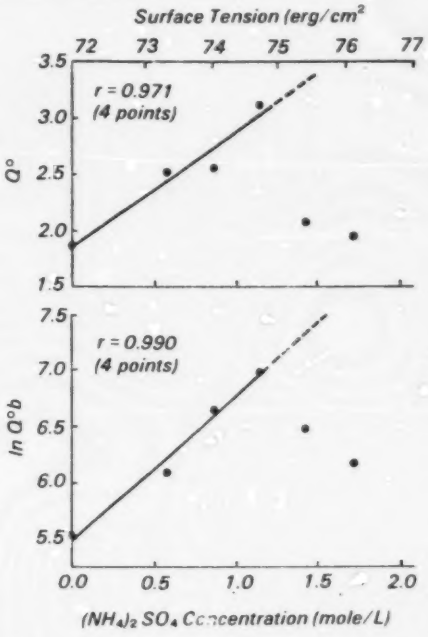


*Figure 3.* *Adsorption capacity and adsorbability versus salt concentration and solvent surface tension for 4-n-propylphenol.*

The adsorption capacity of carboxylic acids exhibit a definite increase as the pH is decreased from 7.00 to 4.75. This can be explained by noting that a low pH increases the relative amount of apolar undissociated carboxylic form. The solvophobic theory is also tested using carboxylic acids at different pH. Correlation with adsorption capacity for the simplified solvophobic theory parameter, TSA, is only in good agreement with theory at pH 7.00. Surface interactions at low pH probably complicate matters.

The solvophobic theory successfully correlates both gas and liquid phase adsorbabilities ($\ln bp_s$ and $\ln Q°b$ respectively) for the alcohols. It also predicts the reversal in order of preferential adsorption with molecular weight because of the presence of liquid water. The complete and simplified $c\phi$ theory is also used to correlate adsorbability from solution for homologous series of alcohols, ketones and phenols. In all three cases, the simplified theory is found to be sufficient, and molecular weight can be ruled out as a correlating parameter for adsorbability.

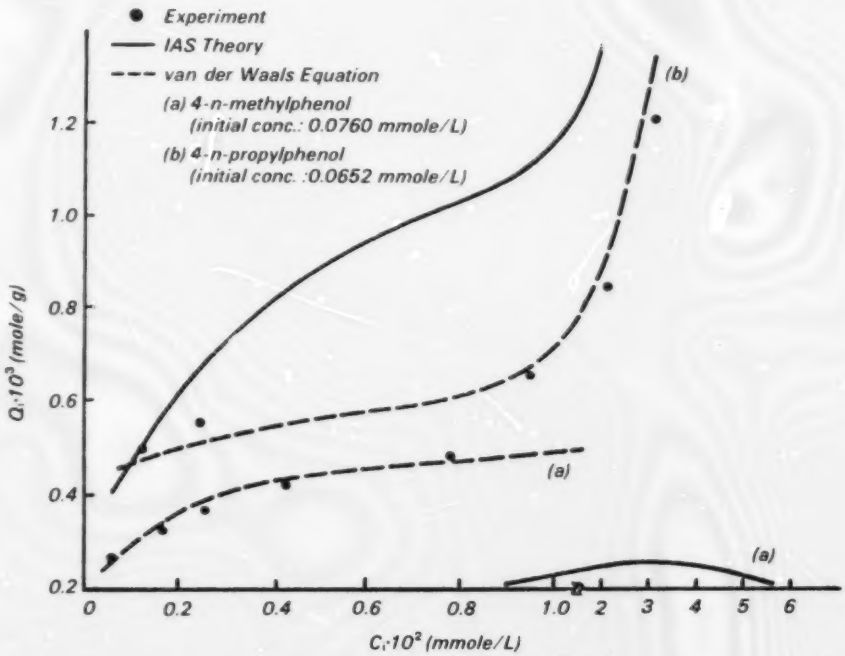


*Figure 4.* *Adsorption from aqueous multi-solute system (4-n-methylphenol and 4-n-propylphenol) at low initial concentrations.*



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The adsorption isotherms of dilute aqueous solutions containing 4-n-methylphenol and 4-n-propylphenol are measured over a concentration range of 0.1 – 0.001 mole/L on activated carbon at 20°C. The experimental results agree better with equilibrium predictions based on a two-dimensional adsorbed phase represented by a van der Waals Equation of state than by an ideal adsorbed solution theory, especially for the weak adsorbate. It appears that the ideal adsorbed solution theory is reliable for multicomponent systems where solute adsorption loading is low. When solute adsorption loading is high, the non-ideality of mixing in the adsorbed phase is related to constants in the two-dimensional equation of state to allow for solute-solute interactions on the surface.

## Recommendations

Myers and Sircar have recently reported an asymptotic principle of correspondence for physical adsorption equilibria on heterogeneous and microporous surfaces. They propose a dimensionless group [mRT ln $(p/p_o)/\Delta G$] as a universal function of $\theta$ (fractional filling of micropores); where m is the saturation capacity and $\Delta G$ is the free energy of immersion of the adsorbent in the pure liquid sorbate. It may be possible to predict $\Delta G$ for homologous series of adsorbate, using the solvophobic theory. In addition to the free energy of immersion approach, gas phase adsorption data have been used in our laboratory to estimate the dispersion contribution of the surface free energy of the adsorbent. Combining the statistical mechanical theories of adsorption from solution with the relationship between interfacial tension and tensions, it can be shown that both the total surface area of the solute and the surface free energy of the adsorbent are important factors for rank-ordering adsorption potential. A linear relationship between total surface area of solute and Gibbs free energy change of adsorption from solution has been demonstrated by the solvophobic theory. Thus a comprehensive experimental data-base of surface free energy for adsorption from the gas phase and its influence on organic adsorption selectivity will provide insight into the adsorption process. This, together with the solvophobic theory, will provide a quantitative description of the role of the solvent and the effects of structural modifications of organic molecules on adsorption.



The full report was submitted in fulfillment of Cooperative Agreement No. CR-809686-01-0 by Rensselaer Polytechnic Institute under the sponsorship of the U.S. Environmental Protection Agency.

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***Richard A. Dobbs** is the EPA Project Officer (see below).*
*The complete report, entitled "Prediction of Selectivity for Activated Carbon Adsorption of Trace Organic (Homologue) Contaminants," (Order No. PB 85-243 160/AS; Cost: $11.95, subject to change) will be available only from:*
*National Technical Information Service*
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